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⑷ **Refrigerator oil composition for fluoroalkane refrigerant.**

⑷ A refrigerator oil composition for a fluoroalkane refrigerant, which comprises a base oil composed principally of an oxygen-containing compound and, based on the total weight of the composition, 0.005-5.0 wt.% of a boron compound as an essential component.

by weight of the refrigerator oil composition and 100 parts by weight of a refrigerant composed of a fluoroalkane.

5 The base oil contained in the refrigerator oil composition according to the present invention is composed principally of an oxygen-containing compound. Any oxygen-containing compound is usable as long as it can be employed as a base oil in refrigerator oils. Specific examples of the compound include esters, polyglycols, polyphenyl ethers, silicates, polysiloxane and perfluoroether. Among them, esters and polyglycols are particularly preferred.

Exemplary esters include dibasic acid esters, polyol esters, complex esters and polyol carbonate esters.

10 Exemplary dibasic acid esters include esters of C₅₋₁₀ dibasic acids, such as glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid, and linear- or branched-alkyl-containing C₁₋₁₅ mono-hydric alcohols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol and pentadecanol. Specific examples include ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate and di-3-ethylhexyl sebacate.

15 As polyol esters, esters of diols or polyols containing 3-20 OH groups and C₆₋₂₀ fatty acids can be used preferably. Specific examples of diols include ethylene glycol, 1,3-propanediol, propylene glycol, 1,4-butane-diol, 1,2-butanediol, 2-methyl-1,3-propanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2-ethyl-2-methyl-1,3-propanediol, 1,7-heptanediol, 2-methyl-2-propyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol and 1,12-dodecanediol. Specific examples of polyols include polyhydric alcohols such as trimethylolethane, trimethylolpropane, trimethylolbutane, di-(trimethylolpropane), tri-(trimethylolpropane), pentaerythritol, di-(pentaerythritol), tri-(pentaerythritol), glycerin, polyglycerins (dimer to eicosamer of glycerin), 1,3,5-pantanetriol, sorbitol, sorbitane, sorbitol-glycerin condensates, adonitol, arabinitol, xylitol and mannitol; saccharides such as xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose, sucrose, raffinose, gentianose and melezitose; partially-etherified products thereof; and methyl glycoside (glycoside). Illustrative fatty acids include linear or branched fatty acids such as hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, eicosanoic acid and oleic acid; and so-called neo-acids having a quaternary α -carbon atom. These polyol esters may contain one or more free hydroxyl groups. Particularly preferred examples of polyol esters include esters of hindered alcohols such as neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, di-(trimethylolpropane), tri-(trimethylolpropane), pentaerythritol, di-(pentaerythritol) or tri-(pentaerythritol). Specific examples include trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol 2-ethylhexanoate and pentaerythritol pelargonate.

20 The term "complex ester" as used herein means an ester of a monohydric alcohol and polyol with a fatty acid and a dibasic acid. As the fatty acid, dibasic acid, monohydric alcohol and polyol, those exemplified above with respect to the dibasic acid ester and polyol ester can be used.

25 The polyol carbonate ester is an ester of a carbonic acid and a polyol. As illustrative polyols, those exemplified above with respect to the polyol ester, polyglycols obtained by homo- or co-polymerization of diols as well as those obtained by adding a polyglycol to the polyols exemplified above can be used.

30 Preferred examples of the polyglycol include polyalkylene glycols, etherified polyalkylene glycols and modified compounds thereof. As polyalkylene glycols, those obtained by homo- or co-polymerization of diols can be used. Usable as diols are those exemplified above with respect to the polyol ester as well as polyalkylene glycols with their hydroxyl group or groups etherified. Specific examples of the groups to be introduced for the etherification of polyalkylene glycols include monomethyl ether, monoethyl ether, monopropyl ether, monobutyl ether, monopentyl ether, monohexyl ether, monoheptyl ether, monoocetyl ether, monononyl ether, monodecyl ether, dimethyl ether, diethyl ether, dipropyl ether, dibutyl ether, dipentyl ether, dihexyl ether, diheptyl ether, dioctyl ether, dinonyl ether and didecyl ether. Illustrative modified compounds of polyglycols include polyol-polyalkylene glycol adducts and etherified products thereof. In this case, the polyols exemplified above with respect to the polyol ester can be used. Incidentally, when the polyalkylene glycol has been obtained by the copolymerization of diols having different structures, no particular limitation is imposed on the manner of polymerization of oxyalkylene groups. The oxyalkylene groups may be copolymerized either at random or in blocks.

35 Although no particular limitation is imposed on the molecular weight of each polyglycol used in the composition of the invention, one having a number average molecular weight of 200-4,000 can be used preferably to further improve the sealing of compressors, with a polyglycol having an average molecular weight of 300-3,000 being more preferred.

40 The oxygen-containing compounds described above can be used either singly or in combination. The kinematic viscosity of the oxygen-containing compound in the present invention is 2-150 cSt, preferably 4-100

Examples of the aminoamide include polyalkylene polyamines each of which have been partially amidated with a fatty acid.

Illustrative benzylamines include those prepared by so-called Mannich reaction, that is, by reacting a polyolefin, such as polypropylene oligomer or polybutene, having a molecular weight of 300-3000 with phenol to yield alkyl phenol and then reacting the resultant alkylphenol with formaldehyde and a polyamine.

Examples of the polyalkenyl amine include those obtained by chlorinating a polyolefin having a molecular weight of 300-3000 such as polybutene and then reacting the chlorinated polyolefin with ammonia, a polyamine or the like.

Examples of the higher alcohol ester compounds include esters of C_{8-20} higher alcohols with C_{8-20} higher fatty acids. Specific examples of the C_{8-20} higher alcohol include octyl alcohol, nonyl alcohol, decyl alcohol, undecyl alcohol, dodecyl alcohol, tridecyl alcohol, tetradecyl alcohol, pentadecyl alcohol, hexadecyl alcohol, heptadecyl alcohol, octadecyl alcohol, nonadecyl alcohol and eicosyl alcohol. Examples of the C_{8-20} fatty acid include octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid and eicosanoic acid.

Usable as boron compounds in the present invention are those obtained by reacting a nitrogen-containing compound such as the dibasic acid imide, aminoamide, benzylamine and polyalkenyl amine each of which have been exemplified above, a higher alcohol ester or the like with a boric acid, borate or boric acid ester, that is, by conducting modification with a boric acid.

Specific examples of the boric acid usable upon the modification include orthoboric acid, metabolic acid and tetraboric acid.

Specific examples of the borate usable upon the modification include alkali metal salts, alkaline earth metal salts and ammonium salts of a boric acid, and more specifically lithium borates such as lithium metaborate, lithium tetraborate, lithium pentaborate and lithium perborate; sodium borates such as sodium metaborate, sodium diborate, sodium tetraborate, sodium pentaborate, sodium hexaborate and sodium octaborate; potassium borates such as potassium metaborate, potassium tetraborate, potassium pentaborate, potassium hexaborate and potassium octaborate; calcium borates such as calcium metaborate, calcium diborate, tricalcium tetraborate, pentacalcium tetraborate and calcium hexaborate; magnesium borates such as magnesium metaborate, magnesium diborate, trimagnesium tetraborate, pentamagnesium tetraborate and magnesium hexaborate; and ammonium borates such as ammonium metaborate, ammonium tetraborate, ammonium pentaborate and ammonium octaborate.

Specific examples of boric acid esters usable upon the modification include esters of a boric acid and, preferably, a C_{1-6} alkylalcohol. Specific examples include monomethyl borate, dimethyl borate, trimethyl borate, monoethyl borate, diethyl borate, triethyl borate, monopropyl borate, dipropyl borate, tripropyl borate, mono-butyl borate, dibutyl borate and tributyl borate.

As boric acid esters, which are the boron compounds according to this invention, boric acid esters with a C_{8-20} higher monoalcohol and those with a C_{8-20} higher polyhydric alcohol can be employed. Specific examples of the ester include boric acid monoesters, boric acid diesters and boric acid triesters with a higher monoalcohol such as octyl alcohol, nonyl alcohol, decyl alcohol, undecyl alcohol, dodecyl alcohol, tridecyl alcohol, tetradecyl alcohol, pentadecyl alcohol, hexadecyl alcohol, heptadecyl alcohol, octadecyl alcohol, nonadecyl alcohol and eicosyl alcohol; those with a higher polyhydric alcohol such as octanediol, nonanediol, decanediol, undecanediol, dodecanediol, tridecanediol, tetradecanediol, pentadecanediol, hexadecanediol, heptadecanediol, octadecanediol, nonadecanediol, eicosanediol, octanetriol, nonanetriol, decanetriol, undecanetriol, dodecanetriol, tridecanetriol, tetradecanetriol, pentadecanetriol, hexadecanetriol, heptadecanetriol, octadecanetriol, nonadecanetriol and eicosanetriol; and mixtures thereof.

Specific examples of the alkali metal salt, alkaline earth metal salt and ammonium salt of a boric acid, which are also the boron compounds according to the present invention, include lithium borate such as lithium metaborate, lithium tetraborate, lithium pentaborate and lithium perborate; sodium borates such as sodium metaborate, sodium diborate, sodium tetraborate, sodium pentaborate, sodium hexaborate and sodium octaborate; potassium borates such as potassium metaborate, potassium tetraborate, potassium pentaborate, potassium hexaborate and potassium octaborate; calcium borates such as calcium metaborate, calcium diborate, tricalcium tetraborate, pentacalcium tetraborate and calcium hexaborate; magnesium borates such as magnesium metaborate, magnesium diborate, trimagnesium tetraborate, pentamagnesium tetraborate and magnesium hexaborate; ammonium borates such as ammonium metaborate, ammonium tetraborate, ammonium pentaborate, ammonium hexaborate and ammonium octaborate; and mixtures thereof. Any of these compounds whether they contain water or crystallization or not are usable. As described above, it is desired to employ, as the boron compound of the present invention, the alkali metal salt, alkaline earth metal salt or ammonium salt of a boric acid after being

jected to a wear test. The results of the test are summarized in Table 1.

(Wear Test)

5 Each refrigerator oil composition and HFC-134a refrigerant were weighed in a high-pressure vessel. The latter, HFC-134a, was weighed to give the refrigerant pressure of 10 kgf/cm². A wear test was conducted in the vessel by employing a disc-shaped test piece and vanes in combination. A set of three vanes was radially installed in contact with the test piece and was rotated. The disc-shaped test piece was fixed on the bottom of vessel and a load was applied upwardly from the bottom of the disc by hydraulic pressure.

10 As the test piece, aluminum (AC8A) and iron (SUJ2) were used.

 The test was conducted at 80°C for one hour at the rotational speed of 3,000 rpm. After the completion of the test, wear resistance was evaluated in accordance with the wear loss (mg) of the vanes.

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Table 1 (2)

Example/ Comp. Ex.	Base Oil	Additive (wt.%)	Wear loss (mg) of vanes After wear test	
			(1)	(2)
Ex. 16	Modified PAG	Compound A (0.05)	17	4.6
Ex. 17	Modified PAG	Compound A (0.5)	15	2.2
Ex. 18	Modified PAG	Compound A (5.0)	15	1.8
Ex. 19	Modified PAG	Compound B (0.1)	15	3.0
Ex. 20	Modified PAG	Compound C (0.1)	17	2.8
Ex. 21	Modified PAG	Compound C (0.1) TCP (1.0)	2.2	2.7
Ex. 22	Modified PAG	Compound D (0.01 as an actual concentration)	18	2.5
Comp. Ex. 1	Ester oil		18	21
Comp. Ex. 2	Ester oil	TCP (1.0)	11	25
Comp. Ex. 3	PAG		20	25
Comp. Ex. 4	PAG	TCP (1.0)	13	28
Comp. Ex. 5	PAG	OAL (3.0)	15	20
Comp. Ex. 6	PAG	MOE (3.0)	18	24
Comp. Ex. 7	Modified PAG		18	19
Comp. Ex. 8	Modified PAG	TCP (1.0)	10	22

(1) Vane (iron: SW2) and disc (aluminum: AC8A) combination
 (2) Vane (aluminum: AC8A) and disc (aluminum: AC8A) combination

As can be understood from Comparative Examples 2, 4 and 8, when TCP was added, the wear loss of iron decreased but that of aluminum showed a rather increasing tendency. When the boron compound A or D according to the present invention was incorporated as shown in Examples, on the other hand, the wear loss of aluminum was extremely small. Even the combined use of the compound with TCP reduced the wear loss of iron without increasing that of aluminum.

As can be seen from Comparative Examples 5 and 6, OAL, MOE and the like which have heretofore been employed as an oiliness improver or friction controller for engine oils did not show any effect even if added to a compression type refrigerator oil which is composed of an oxygen-containing base oil and used in the form of a mixture with a fluoroalkane refrigerant. It is apparent, however, that the combined use of the boron com-



EUROPEAN SEARCH REPORT

Application Number
EP 93 30 6100

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.CLS)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	WO-A-91 15551 (LUBRIZOL) * the whole document * ---	1-10	C10M171/00 C10M169/04 C09K5/04 //C10M139/00, C10N60/14
X	EP-A-0 470 788 (NIPPON OIL) * the whole document * ---	1-10	
X	EP-A-0 452 816 (NIPPON OIL) * the whole document * ---	1-10	
X	EP-A-0 113 045 (HONDA MOTOR CO.)	1-8	
Y	* the whole document * ---	9,10	
X	EP-A-0 039 998 (EXXON)	1-8	
Y	* page 8, line 16 - line 23 *	9,10	
Y	EP-A-0 426 153 (MITSUI PETROCHEM. IND.) * the whole document * ---	9,10	
A	DATABASE WPI Week 8403, Derwent Publications Ltd., London, GB; AN 84-015004 & JP-A-58 208 375 (MATSUSHITA ELEC. IND.) * abstract * -----	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C10M
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		29 October 1993	DE LA MORINERIE, B
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : co-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			